DEMETALLATION OF WASTE OIL WITH COAL

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INTRODUCTION

The breakdown of coal into liquid fuels has been researched extensively in order to improve upon the economics of the process. To produce liquid fuels from hydrogen deficient coal, hydrogen must be added. Weisz noted that for the most hydrogen deficient coals, it would be necessary to add 8 % by weight hydrogen to produce quality hydrocarbons.[1] One way to decrease the cost of coal liquefaction would be to minimize the need for expensive hydrogen. By coprocessing coal with heavy petroleum resids, the resid may act as a hydrogen donor for the coal diminishing the need for additional costly hydrogen gas.[2] In coprocessing resids with coal it has also been shown that some of the nickel and vanadium that are naturally abundant in the resid reside in the coal char and ash after coprocessing.[3]

More recently, it has been shown that coprocessing waste materials (plastics, rubbers, and waste lubricants) with coal can decrease the cost of coal liquefaction.[4] In addition, coprocessing of coal with waste materials has also been shown to enhance coal conversion to liquids.[5] The addition of waste materials to coal liquefaction reactions also means the addition of heavy metals. Waste rubber tires contain zinc[6] and waste lubricants can contain a variety of heavy metals such as iron, manganese, and zinc.[7] Recent results indicate trace heavy metals found in waste automotive oil will reside in coal char and ash after coprocessing.[7] Demetallation of the trace heavy metals in waste automotive oils was not found to be dependent upon the rank of coal. Out of six different coals used in the demetallation experiments, Illinois #6 coal showed the best demetallation effect. The Illinois #6 has a high content of inorganic matter which has been suggested to have influence on the degree of demetallation. The present paper reports further experiments carried out with Illinois #6 and demineralized Illinois #6 in order to determine the effect of the inorganic portion of the coal on demetallation of waste automotive oil. The extent of the demetallation of the produced oil is reported. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of the coals before and after demineralization.

EXPERIMENTAL

Illinois #6 was obtained from the Pennyslvania State Coal Sample Bank. The Illinois #6 was used as received (-60 mesh). At all times the coal was stored under a nitrogen atmosphere. The waste automotive oil was obtained from Interline Resources Inc. (Salt Lake City, Utah). The waste automotive oil was stored under ambient conditions and used as received. Demineralization of the Illinois #6 coal was carried out by mixing 500 mL of 6 N HCl with 20 g of Illinois #6 at approximately 45 °C for 1 hour. The coal was then filtered. The filtered coal was then mixed with 250 mL of concentrated HF at ambient conditions for 1 hour. The coal was again filtered. The coal was then treated with 250 mL of 12 N HCl at 45 °C for 1 hour. The coal was then filtered and washed with deionized water until no chloride was precipitated by addition of silver nitrate. The demineralized coal and the untreated coal were dried at 100 °C under vacuum for 2 hours. The dried demineralized and dried untreated coal were then mixed with waste automotive oil in a 1:1 ratio determined by weight. Samples were placed in stainless steel tubing reactors which have volumes of 27 cm^3. Tubing reactors were sealed and then purged with nitrogen gas and finally pressurized to 1000 psig (cold) of hydrogen. Tubing reactors were placed in a fluidized sandbath and shaken vertically at a rate of 160 rpm. The temperature of the sandbath was maintained at 430 °C for 1 hour. After liquefaction the tubing reactor was removed from the sandbath and cooled at room temperature for 5 minutes and finally quenched in cold water. The sample was scraped out of the tubing reactor and placed in a Soxhlet extraction thimble. The internal surfaces of the

tubing reactor were washed with tetrahydrofuran (THF). The THF wash was then placed in the before mentioned extraction thimble. The material was then extracted with THF using a Soxhlet extractor for 48 hours. The nonsoluble portion was dried and weighed in order to calculate the total conversion on a dry ash free. The THF soluble portion was run through a rotary evaporator to remove the THF. The THF soluble portion was then dried under vacuum at 430 °C for 2 hours. The THF soluble portion was extracted with cyclohexane. The portion that is insoluble in cyclohexane is referred to as asphaltenes. The cyclohexane was removed from the cyclohexane soluble portion with a rotary evaporator. The residue was then dried under vacuum at 100 °C for 2 hours. The cyclohexane soluble portion is referred to as oil. The ICP analyses were completed by Data Chem Laboratories, Salt Lake City, UT. The XPS results were obtained from a FISONS ESCALAB 220i-XL using a six channel detection system. Samples were mounted upon double sided 3M tape on top of a metallic sample holder. Charging effects were countered by using an electron flood gun.

RESULTS

Proximate and ultimate analyses of the untreated Illinois #6 coal are given in Table 1.[8] The Illinois #6 coal is a high volatile C bituminous coal. Table 2 shows a comparison of ICP analyses of untreated coal and demineralized coal. There is a significant difference in the amount of inorganic matter present in the untreated coal and the demineralized coal. Table 2 shows a substantial decrease in naturally abundant metals such as aluminum, calcium, iron, and sodium for the demineralized coal. This indicates that the demineralization process was effective in removing a substantial fraction of the inorganic constituents.

XPS analysis of the untreated and the demineralized Illinois #6 coal indicates a decrease in inorganic matter at the surface of the demineralized coal. The XPS analysis of the untreated Illinois #6 coal detected sodium, aluminum, silicon, sulfur, and calcium. XPS analysis of the demineralized coal detected only sulfur and calcium. This indicates that some of the inorganics on the surface of the coal were effectively removed by the demineralization process. From the ICP result, iron makes up over 2 % by weight of the total Illinois #6 coal. Detection of the iron by XPS was not achieved. Past investigators have also reported that detection of iron on the surface of coal is difficult.[9,10] We assume that most of the iron present resides in the bulk coal structure and not upon the coal surface.

The waste automotive oil was analyzed by ICP to determine the type of trace heavy metals present. The results are shown in Table 3. The phosphorous and zinc are present due to an antiwear lubricant, zinc dialkyldithiophosphate, added to the motor oil.[11]

Table 4 shows the liquefaction conversion data for reacting untreated Illinois #6 and demineralized Illinois #6. The untreated Illinois #6 showed better total conversion than the demineralized coal probably because of the decrease in iron in the demineralized coal. Decreasing the iron content decreases the pyrrhotite formation. Pyrrhotites are known to act as coal liquefaction catalysts.[12]

The last two columns of Table 3 shows the ICP analysis of the product oils or the cyclohexane soluble portion of the coal and waste automotive oil reactions. The product oil from both the untreated and the demineralized coal are free of all the elements detected in the untreated waste automotive oil except for some sodium detected in the oil sample from the demineralized coal.

Demineralization of the Illinois #6 decreased the inorganic portion of the coal substantially. The iron content was decreased from 2.3 % to 1.5 % yet the presence of 1 % iron or more would still be sufficient enough for catalytic effects.[13] The remaining iron in the form of iron sulfide will function as a catalyst aiding in dissolution of the coal forming gas, oil, asphaltenes, and char. In coprocessing experiments conducted with resids, Miller et al. concluded that new char formation was responsible for demetallation.[14] In past studies completed in this laboratory, trace heavy metals initially in the automotive oil were found to be more abundant in

asphaltenes.[7] The asphaltenes are precursors to char. Retrogressive reactions allow asphaltenes, laden with heavy metals, to form char which may then trap or embed the heavy metals. Therefor, iron sulfide enhances formation of asphaltenes and indirectly char which traps heavy metals. Thus the iron inherent in the coal may aid in demetallation of the waste automotive oil.

CONCLUSION

Demineralized Illinois #6 coal showed no detectable difference for demetallation of waste automotive oil in coprocessing reactions when compared to untreated Illinois #6 coal. The inorganic portion of the coal, except the iron, seems to have little effect upon the demetallation characteristics of the coal.

ACKNOWLEDGMENTS

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Table 1 Proximate and Ultimate Analysis of Coals From Pennyslvania State Coal Sample Bank

	Illinois #6
Proximate	
% Ash	16.16
% Volatile	38.14
% Fixed Carbon	45.70
Ultimate	
% Carbon	78.11
% Hydrogen	5.44
% Nitrogen	1.32
% Sulfur	5.39
% Oxygen	9.73
Iron	
% Iron	2.3

Table 2 ICP analyses of untreated Illinois #6 coal and demineralized Illinois #6 coal

Metal	Illinois #6 µg/g	Demineralized Illinois #6 µg/g
Aluminum	1,300	330
Antimony		
Arsenic		
Barium	17	6.6
Beryllium	1.1	.8
Cadmium	1.2	.6
Calcium	6100	320
Chromium	14	15
Cobalt	5.6	
Copper	10	11
Iron	23,000	15,000
Lead	10	
Lithium		
Magnesium	220	42
Manganese	58	13
Molybdenum		
Nickel	14	14
Phosphorous		
Potassium	460	
Selenium		
Silver		
Sodium	770	160
Strontium	24	12
Thallium		
Vanadium	19	20
Zinc	74	4.3

Table 3 First column contains ICP analysis of the received waste automotive oil. The second and third columnss are ICP analyses of oils produced from reacting waste automotive crankcase oil with untreated Illinois #6 coal and demineralized Illinois #6 coal at 430 °C under a 1000 psig (cold) hydrogen for 1 hour.

Metal	Waste Automotive Oil µg/g	Untreated Illinois #6 Coal Oil µg/g	Demineralized Illinois #6 Coal Oil µg/g
Aluminum			
Antimony			
Arsenic			
Barium	11		
Beryllium			
Cadmium			
Calcium	990		
Chromium	2.7		
Cobalt			
Copper	44		
Iron	130		
Lead	47		
Lithium			
Magnesium	410		
Manganese	10		
Molybdenum			
Nickel			
Phosphorous	780		
Potassium			
Selenium			
Silver			
Sodium	450		76
Strontium			
Thallium			
Vanadium			
Zinc	690		

Table 4 Percent conversion of untreated Illinois #6 and demineralized Illinois #6 coal reacted with waste automotive oil mixed in a 1:1 ratio by weight. Liquefaction was carried out in tubing reactors at 430 °C under a 1000 psig (cold) hydrogen for 1 hour.

	Untreated Illinois #6	Demineralized Illinois #6
Gas + Oil	38.8	40.2
Asphaltenes	22.1	13.2
Total Conversion	60.9	53.4